Bulk Electronic Structure of BiFe_{1-x}M_xO₃ (M=Mn and Co) Thin Films by Soft-X-Ray Spectroscopy

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Multiferroic BiFeO₃ has a rhombohedrally distorted perovskite structure, which belongs to the space group *R3C* with the unit cell parameters a=3.96 Å and $\alpha=89.4$ °. BiFeO₃ is a suitable candidate material for attaining ferroelectric and antiferromagnetic domain couplings at room temperature (RT), owing to its high Curie temperature of ~1100K and its high Neel temperature of ~643K. This material can expect as application of ferroelectric or magnetic memory device on thin film form. Major problem for BiFeO₃ thin film is large leakage current and coercive field, which affects the measurement of ferroelectricity at RT. This originates the mixed valence states of Fe ions (Fe²⁺ or Fe³⁺) that were created by oxygen vacancies for charge compensation. Naganuma and co-workers have prepared the Mn, Co doped BiFeO₃ thin films by CSD and characterized their magnetric and ferroelectric properties [1]. The Co-doped BiFeO₃ thin film decreases the coercive field (*E_c*) without reducing remanent polarization. They have reported that the Co substitution is effective for the improvements of ferroelectric and magnetic properties of BiFeO₃ thin film [1].

In this study, the electronic structure of $BiFe_{0.96}Mn_{0.04}O_3$ and $BiFe_{0.96}Co_{0.04}O_3$ thin films have measured the electronic structure using X-ray absorption spectroscopy (XAS) and soft-X-ray emission spectroscopy (SXES). In this paper, the authors discuss that the electronic structure and energy gap is closely related with the ferroelectricity (or leakage current) of BiFeO₃ thin film.

 $BiFeO_3$ and $BiFe_{0.96}M_{0.04}O_3$ (M=Mn, Co) thin films were fabricated by chemical solution deposition (CSD) on Pt/Ti/SiO₂/Si substrates. Postdeposition annealing was performed by a rapid thermal annealing at 873 K in air. The film thickness was 180-220 nm. These thin films were characterized by X-ray diffraction measurement.

The X-ray absorption spectroscopy (XAS) and SXES spectra were carried out at the undulator beamline BL-19B at the Photon Factory (PF) of the High Energy Accelerator Organization (KEK). The energy resolution was higher than 0.2 eV at hv=700 eV. The energy axis was calibrated by measuring the 4*f* core level of an Au film deposited in situ on the sample

substrate.

Figure 1 shows the Fe 2p XAS spectra of BiFeO₃, BiFe_{0.96}Mn_{0.04}O₃ and BiFe_{0.96}Co_{0.04}O₃ thin films. As reference, the Fe 2p XAS spectrum of LaFeO₃ with the valence state of Fe³⁺ is also shown. The Fe 2p XAS corresponds to the transition of electron from Fe 2p core level to unoccupied Fe 3d state. The spectrum of LaFeO₃ consists of two parts of derived from the spin-orbit split of L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) states. They are further split into the t_{2g} and e_g states of Fe 3d due to the octahedral ligand field. The crystal field splitting (10Dq) corresponding to the energy separation between t_{2g} and e_g states is 1.4 eV. The spectral shape, peak positions and 10Dq of BiFeO₃ are



Fig. 1: Fe 2*p* XAS spectra of BiFeO₃, BiFe_{0.96}Mn_{0.04}O₃ (Mn-BiFeO₃) and BiFe_{0.96}Co_{0.04}O₃ (Co-BiFeO₃) thin films.

similar to those of LaFeO₃, which was theoretically calculated assuming a high-spin $t_{2g}{}^3 e_g{}^2$ ground state. Furthermore, the peak positions of BiFe_{0.96}Mn_{0.04}O₃ and BiFe_{0.96}Co_{0.04}O₃ thin films accord with those of BiFeO₃ and LaFeO₃. These results indicate that the BiFe_{0.96}Mn_{0.04}O₃ and BiFe_{0.96}Co_{0.04}O₃ thin films have the valence state of Fe³⁺ [2].

Figure 2(a) shows the O 1s and Fe 2p SXES spectra and 0 1*s* XAS spectrum of $BiFe_{0.96}Mn_{0.04}O_3$ thin film. The O 1s and Fe 2p SXES spectra were measured at the excitation energies of 540 eV and 740 eV, respectively. The Fe 2p and O 1s SXES spectra, which correspond to fluorescence spectra, reflect the Fe 3d and O 2pPDOS, respectively, in the valence band. The energy position of O 2p state overlaps with that of Fe 3d state. This result indicates that the Fe 3dstate hybridizes with O 2p state in the valence band. The O 2p valence band has three structures labeled as A, B and C. The Fe 3d contribution is more significant in the B and C peaks, where the O 2p states have a larger admixture of Fe 3d states. The A peak corresponds to the O 2p states, which are not hybridized with the Fe derived states. On the other hand, from the dipole selection rules, it is understood that the O 1s XAS spectrum of Fe oxides corresponds to transitions from O 1s to O 2p. The conduction band has three structures shown as dashed curves from Gaussian fitting. The a and b peaks correspond to the t_{2g} and e_{g} states, respectively, of Fe 3d state. The c peak is considered to be Bi 6sp state. The energy separation between a and b peaks accords with the result of Fe 2p XAS spectrum in Fig. 1. The energy gap corresponding to the energy separation between the top of the valence band and the bottom of the conduction band is estimated to be ~ 1.3 eV by concerning the resolution in this measurement system. These band structures accords with those of BiFeO₃ bulk crystal [2].

Figure 2(b) shows the O 1s and Fe 2p SXES spectra and O 1s XAS spectrum of BiFe_{0.96}Co_{0.04}O₃ thin film. The spectral shape and hybridization



Fig. 2: Valence bands and conduction bands of (a) $BiFe_{0.96}Mn_{0.04}O_3$ (Mn-BiFeO₃) thin film and (b) $BiFe_{0.96}Co_{0.04}O_3$ (Co-BiFeO₃) thin film presented on a relative energy compared to E_F . The energy separation between the top of the valence band and the bottom of conduction band reflects the energy gap (E_g) of BiFeO₃.

state of BiFe_{0.96}Mn_{0.04}O₃ thin film are similar to those of BiFe_{0.96}Co_{0.04}O₃ thin film in Fig. 2(a). However, the existence of peak A of the valence band disappears and the energy gap increases. The energy gap is estimated to be ~2.3 eV. In term of the ferroelectricity, the BiFe_{0.96}Co_{0.04}O₃ thin film decreases the coercive field without reducing remanent polarization. This originates that the BiFe_{0.96}Co_{0.04}O₃ thin film has high electrical resistivity. The increase of energy gap is closely related with the decreases E_c .

References

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